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NEW EXPERIENCES WITH EXPLOSION CLAD ALLOYS UNS N06058 AND UNS N06059

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ABSTRACT

Prior work showed that the Ni-Cr-Mo alloys UNS N06058 and UNS N06059 can be reliably explosion clad to carbon steel and are fully compliant with ASME Code. Additionally, corrosion tests in hydrochloric and sulfuric acid, in "green death solution" and further mechanical tests according to SA 265 (Nickel and Nickel-Base Alloy-Clad Steel Plate) have been conducted.

To fabricate equipment such as pressure vessels, explosion cladding is followed by shell and head forming. If requested by the codes, a post weld heat treatment may also be mandatory. After this sequence, the clad bond zone layer has been investigated with respect to mechanical properties and corrosion resistance.

Therefore, best practices for explosive cladding and head forming were identified and evidence was provided that the explosive cladding process does not affect the above-mentioned properties of Ni-Cr-Mo materials. The effect of the post weld heat treatment on the corrosion properties in hydrochloric and sulfuric acid was also investigated and differences between alloy UNS N06058 and alloy UNS N06059 could be detected.

Key words: explosion cladding, explosion welding, Ni-Cr-Mo alloys, UNS N06058, UNS N06059, corrosion resistance, heat treatment, thermal stability, sensitization, shear strength, vessel head forming, DetaClad, plating, hydrochloric acid, sulfuric acid

INTRODUCTION

Classification of the used clad materials and motivation for explosion clad trials

The alloys used as clad material for this study are members of the so-called "C-family". It consists of Ni-Cr-Mo alloys, which are known for combining the corrosion resistance of Ni-Cr alloys in oxidizing media with corrosion resistance of Ni-Mo alloys in reducing media. As a result, these materials have proven to be extremely durable in a wide range of highly aggressive media. The development of these materials started in the 1930s with Alloy C. This alloy showed remarkable corrosion resistance in a wide spread of media, low sensitivity for pitting or crevice corrosion and virtual immunity to chloride induced stress corrosion cracking[1-2].

With these properties, the alloy was well suited for applications in the chemical process industry, oil refining equipment, petrochemical equipment and many more applications in highly aggressive media. With the increasing demands in these application fields, new alloys needed to be explored by using new production processes such as the VOD (vacuum oxygen decarburization). Thus, purer materials could be produced leading to the development of alloys like UNS N06022 and UNS N10276 (nominal compositions see Table 1). These new materials were characterized by lower contents in carbon and silicon resulting from the new production-methods. By that, the binding of chromium in carbides could be decreased and the chromium content in the microstructural matrix was elevated. This resulted in a positive effect on corrosion resistance[1-2].

Further development and increasing demands of the industry finally lead to the introduction of UNS N06059 and UNS N06058[2].

Table 1: Several nickel-chromium-molybdenum alloys of the C-family in order of their introduction as well as their nominal chemical composition and their Pitting Resistance Equivalent Number (PREN); adapted and updated from[2].

Denomination			Introduced	Main alloying elements, typical values, wt%					PREN[*]
Alloy	EN	UNS		Ni	Cr	Mo	Fe	Other	
C-276	2.4819	N10276	1960s	57	16	16	6	3.5 W	75
22	2.4602	N06022	Mid 1980s	56	22	13	4	3 W	70
59	2.4605	N06059	Early 1990s	59	23	16	1		76
2120	2.4700	N06058	Early 2010s	59	21	19	≤1	0.075 N	86
[*]PREN = %Cr + 3.3 (%Mo + 0.5 %W) + 30 %N									

The **UNS N06059**, VDM® Alloy 59[(1)], is the purest ternary alloy of the Ni-Cr-Mo alloys. The nominal composition is limited to the elements Ni (59%), Cr (23%) and Mo (16%), with an iron content below 1%. After its development in the 1990s, it had the highest PRE number of 76 in the C family. The chosen composition gives the alloy excellent resistance in reducing as well as in oxidizing media. In addition, it is also very resistant to localized corrosion such as pitting or crevice corrosion. Compared to the previous representatives of the C-family, UNS N06059 represents a significant improvement in resistance to uniform and local corrosion in a wide range of media. Figure 1 depicts the behavior of UNS N06059 and UNS N06022 in reducing media such as sulfuric acid and hydrochloric acid. Especially in the critical temperature range above 60 °C for highly concentrated sulfuric acid, the corrosion rate of UNS N06059 increases only moderately compared to UNS N06022[3-6].

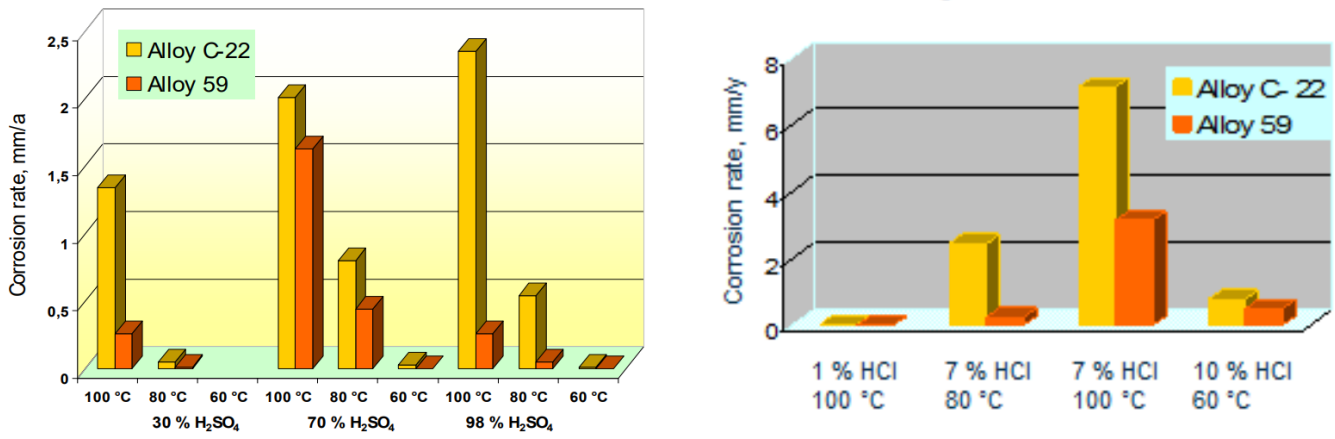[(1)] VDM® Alloy 59 is a registered trade mark by VDM Metals International GmbH

Figure 1: Corrosion tests carried out using UNS N06059 and UNS N06022 in sulfuric acid (left) and hydrochloric acid (right).

The thermal stability of the alloy is also excellent due to the absence of alloying elements such as W and Fe. In comparison with other representatives of the C-family, sensitization, as defined after exceeding an intergranular attack of 50 µm (IC-criterion) for the ASTM G28 A test, only occurs after two hours. In contrast, UNS N10276 already shows signs of sensitization effects after a few minutes (see Figure 2)[7].
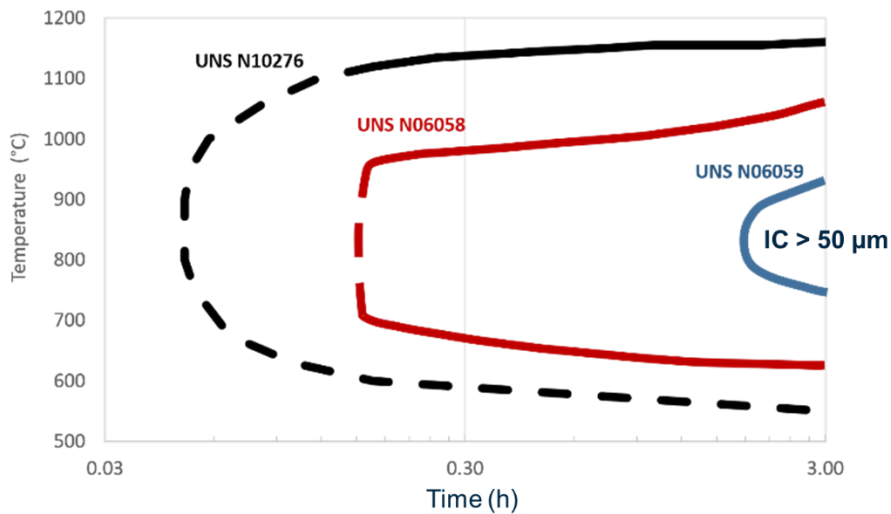

Figure 2: Sensitization curves of selected alloys from the C-family according to the IC-criterion (intergranular corrosion > 50 µm) of the ASTM G28 A test; taken and updated from[8]. Inside the depicted areas, values of mass loss or intergranular attack indicate damaged grain structures in the microstructure.

This results in a wide processing window, which underlines the good fabricability of the alloy. Thus, it is also possible to apply multilayer welds or necessary heat treatments with lower risk of sensitization of the microstructure. A matching filler material is used for welding. The AWS (American Welding Society) and German TÜV have qualified it for all common welding processes[9-10].
These properties make it compatible with the production of chlorinated and fluorinated chemicals, production of HF, HCl-releasing drying processes or electricity carrying rolls in the electrolytic galvanizing of steel strip and many others, such as flare booms in the combustion of chlorinated hydrocarbons or multipurpose plants[7, 11-12].

The alloy **UNS N06058**, VDM® Alloy 2120 MoN[2], is a further development of UNS N06059 and was introduced to the market in the early 2010s. This alloy is not only one of the youngest members of the C-family, but also the only alloy of this group to which nitrogen has been intentionally alloyed. The nominal composition can be seen in Table 1 and ensures that UNS N06058 achieves the highest PRE number in its class with 86. This is particularly due to the high molybdenum content of almost 19 wt. %. As a result, the material shows excellent corrosion resistance in both strongly reducing and oxidizing media. Investigations[13] have also shown that the resistance to pitting and crevice corrosion are excellent (see Figure 3)[13-15].

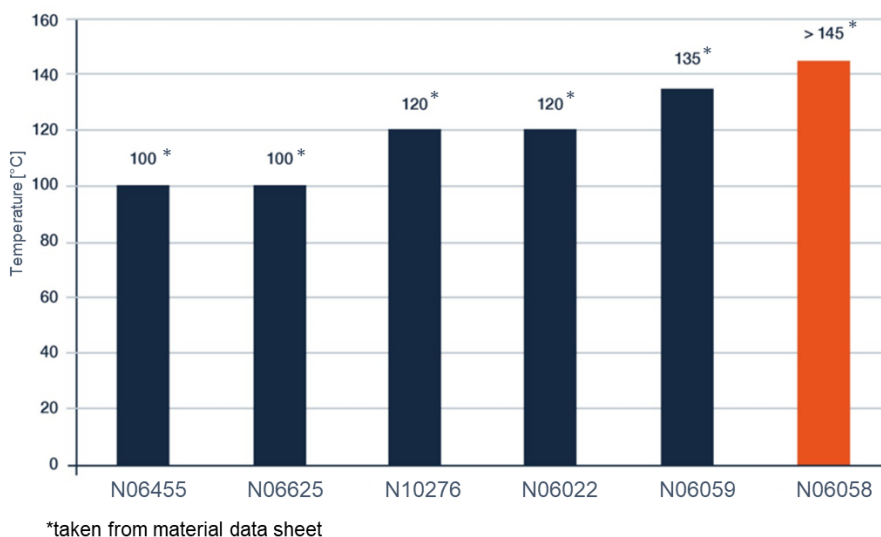*taken from material data sheet

Figure 3: Critical pitting temperature in green death solution for selected alloys.

According to Figure 2, the thermal stability of UNS N06058 differs from that of UNS N06059, due to the materials faster sensitization kinetics. With respect to the IC-criterion of ASTM G28 A, a sufficiently large temperature window to enable good fabricability is given for this material. The significantly increased corrosion resistance resulting from the optimized composition makes the alloy particularly interesting for applications in the chemical process industry, flue gas desulphurization and others, where resistance in highly aggressive media and against pitting and crevice corrosion is required[16].

The matching filler metal cannot only be used to weld UNS N06058 in accordance with the material, but it can also be used as an overalloyed filler metal for other materials. The filler metal is qualified according to AWS 5.14 and VdTÜV-Kennblatt for welding consumables 18954, 18965 and 18953[16].

Preliminary investigations[17] have shown that both alloys UNS N06058 and UNS N06059 can be explosion welded (here referred to as explosion cladding) to carbon steel in accordance with the requirements. During these investigations, matching parameters for head forming and the post weld heat treatment could be evaluated. The explosion cladding process is a high-speed welding operation similar to pressure welding with the difference that the bond zone is much thinner compared to conventional welding. In this process, a plate, which is the clad material, is bonded to a base plate[18].

Basically, the clad material has different properties than the base material. In this case, the clad material has a higher corrosion resistance, while the base material, a low-alloyed carbon steel, is characterized by its strength. For a successful bonding of the plates, the clad plate is covered with explosives and positioned at a short distance from the base plate. Starting from the initiation point, the explosion is then set off, thus converting the chemical energy into kinetic energy, which leads to the top plate's acceleration

towards the base plate. When the two plates meet, the material is bonded at the interface. The process is shown in Figure 4[18-19].
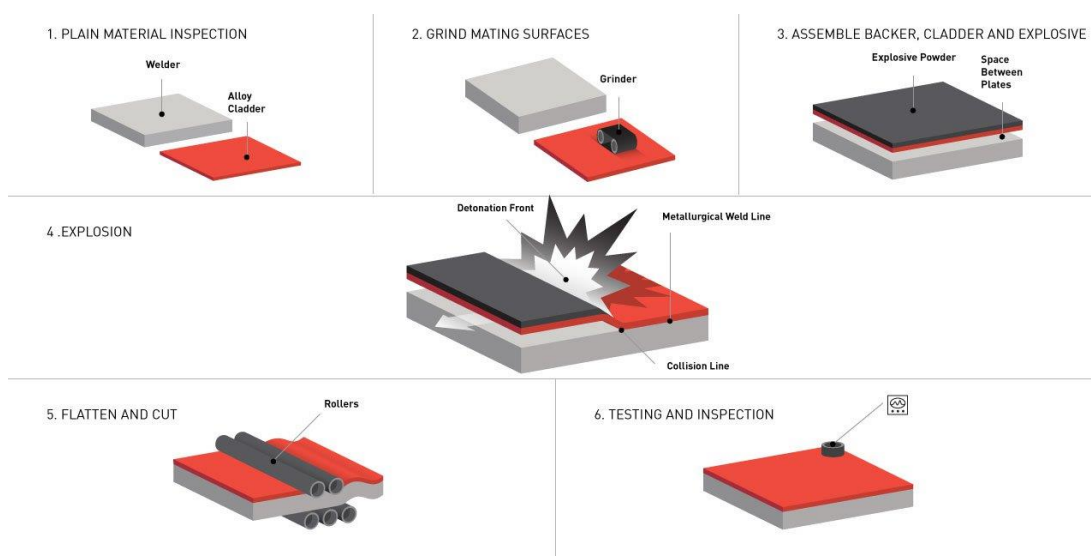

Figure 4: Simplified illustration of the DetaClad™[(3)] explosion welding process (here referred to as explosion cladding) at NobelClad taken from[20].

The advantage of this process lies, among other aspects, in its cost efficiency. Equipment manufactured in this way are more cost-effective than equipment made of solid material from a thickness of 10 - 12 mm (0.39 – 0.47 in). Furthermore, desired material properties can be combined in this way.
This process is used in the production of pressurized vessels piping and/or heat exchangers that exceed a thickness of 12 mm (0.47 in). The relevant parameters for the explosion cladding process are given as explosion velocity, explosion energy and plate separation distance[18-19].

EXPERIMENTAL PROCEDURE

Explosion cladding and head forming

To investigate the properties of explosion clad plates of the alloys UNS N06058 and UNS N06059 in more detail, one plate of each material with the dimensions 1000 x 2000 x 6 mm was seam welded in the center to form a plate of 2000 x 2000 x 6 mm. The matching filler metal UNS N06058 was used for this purpose. Producers qualified in accordance with ASME Code Section IX, using the GTAW process, performed the weld. The seam was welded without any problems and no defects were identified during penetrant testing or X-ray examination. This way it could be ensured that the two materials were exposed to exactly the same process conditions.

The welded plate was then explosion clad onto the base metal ASME/ASTM SA-516-70 carbon steel with dimensions 2000 x 2000 x 25.4 mm. The plate has been cladded using DetaClad™[(3)], the proprietary explosion welding process at NobelClad. After cladding and flattening, an ultrasonic inspection was performed in accordance with ASME/ASTM SA-265 Class 1 specification. No defects were identified.

After a head blank with a diameter of about 1635 mm (64 in) was cut from the plate, the so-called head has been successfully formed at the company König & Co GmbH in Germany (see Figure 5). During the head forming process the material was annealed at 620 °C for 1.35 h and air cooled two times. A sketch

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[3] Detaclad™ is a registered trademark by Nobel Clad GmbH

of the final head is shown in Figure 6. Beforehand, tests with both alloys in the conditions *as clad* and after a *simulated heat treatment* of both the *head forming* process and the *post weld heat treatment* were performed in order to confirm the used processing window for the subsequent head forming of the cladded plate, so that a sensitization of the microstructure should be avoided.
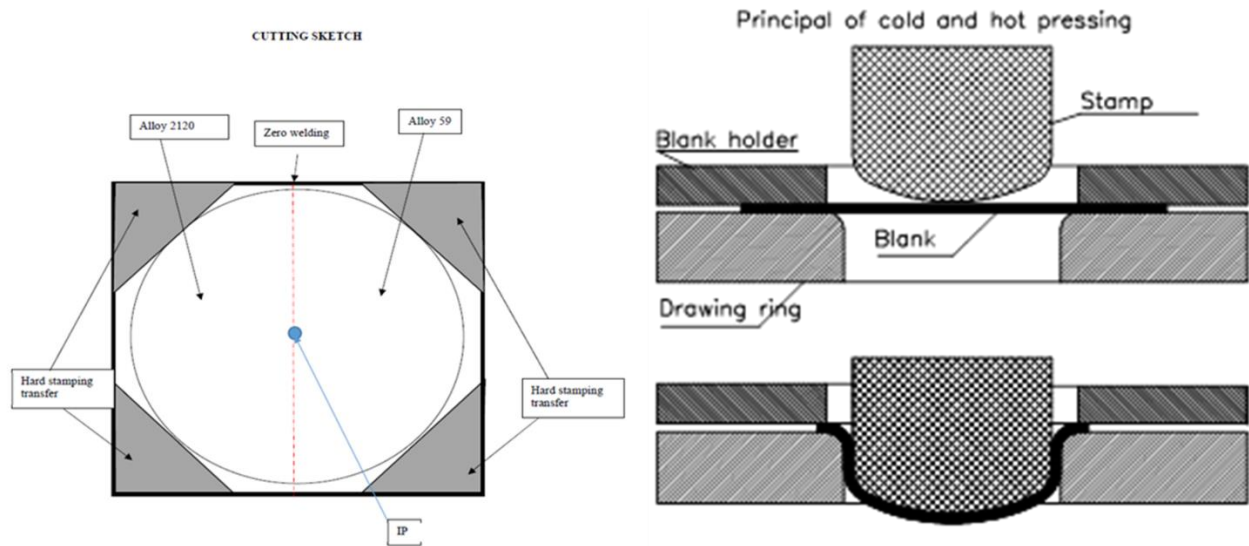

Figure 5: The sketch on the left hand side depicts the head blank that was cut out of the bond for further head forming. On the right hand side, the head forming process is schematically presented.

Test coupons were taken in the "*as clad*" and "*after head forming*" conditions (see Table 2). For this purpose, strips measuring 300 x 20 mm were cut out following Figure 6 and prepared for the subsequent tests. In the condition *after head forming*, test coupons were taken from different regions of the head to check whether the degree of deformation and the different induced strains during head forming have an influence on the properties of the material. In order to simulate a post weld heat treatment (PWHT) of the head after the forming process, duplicates of the coupons in the *after head forming* condition were subjected to an appropriate heat treatment at 600 °C for 13.5 h with air cooling. This corresponds to the maximum duration of a possible PWHT.

Table 2: Depiction of the individual specimen's conditions linked with the stages.

Stage	Condition
1	Delivery condition of raw material (solution annealed)
2	As clad
3	After head forming
4	After head forming + heat treatment (PWHT)

Investigations on mechanical properties and corrosion resistance

The mechanical tests according to ASTM included shear tests, ductility bend tests and tensile tests according to ASTM SA 265. The conditions *as clad* as well as all sampling points of the conditions *after head forming* and *after head forming + heat treatment* were tested.
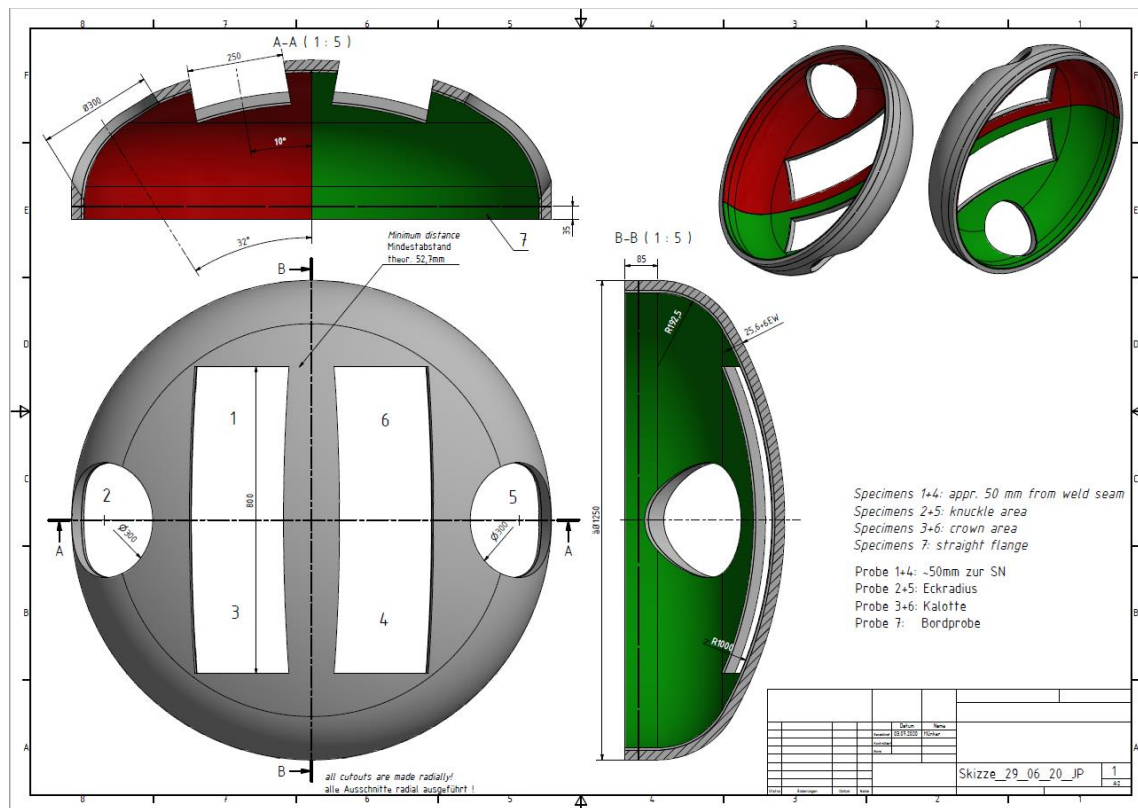
Figure 6: Clad head and positions of the sampling.

As part of the corrosion tests, the conditions depicted in Table 3 were tested in the media mentioned below. To prepare the clad material samples for the corrosion measurements, the carbon steel was removed by milling.

Table 3: Test method and condition of the material.

	Solution annealed	As clad	After head forming	After head forming + heat treatment
Green death solution	x		x	x
ASTM G28 A, 24 h	x	x	x	x
10 % HCl, 60 °C, 24 h	x	x	x	x
50 % H$_2$SO$_4$, 100 °C, 24 h	x	x	x	x

As part of the corrosion properties, the critical pitting temperature was investigated. Thus, the aggressive green death solution, consisting of 11.6 wt.% H_2SO_4 + 1.2 wt.% HCl + 1 wt.% $CuCl_2$ + 1 wt.% $FeCl_3$, was used at a starting temperature of 80 °C. After a testing period of 24 hours, the specimens were examined and if no signs for pitting corrosion could be detected, the test was repeated at a temperature increased by 5 °C until the specimen failed.

For the test method according to ASTM G28 A (50 % H_2SO_4 + 42 g/l $Fe_2(SO_4)_3$ x $9H_2O$, boiling, 24 hours) the mass loss rates of prepared coupons were calculated. Metallographic examinations were carried out afterwards in order to determine the depth of the intergranular corrosion attack.

Furthermore, tests in 10 % HCl at 60 °C and in 50 % H_2SO_4 at 100 °C using testing periods of 24 hours were conducted in order to determine the mass loss rates. These highly reducing acids were deliberately used to investigate the behavior of the tested materials under extreme conditions.

RESULTS AND DISCUSSION

Metallographic investigation of the microstructure

After the bonding process, the explosion clad interface was metallographically inspected, as shown in Figure 7. The inspection revealed a wavy interface, which is very typical for the used bonding mechanism.
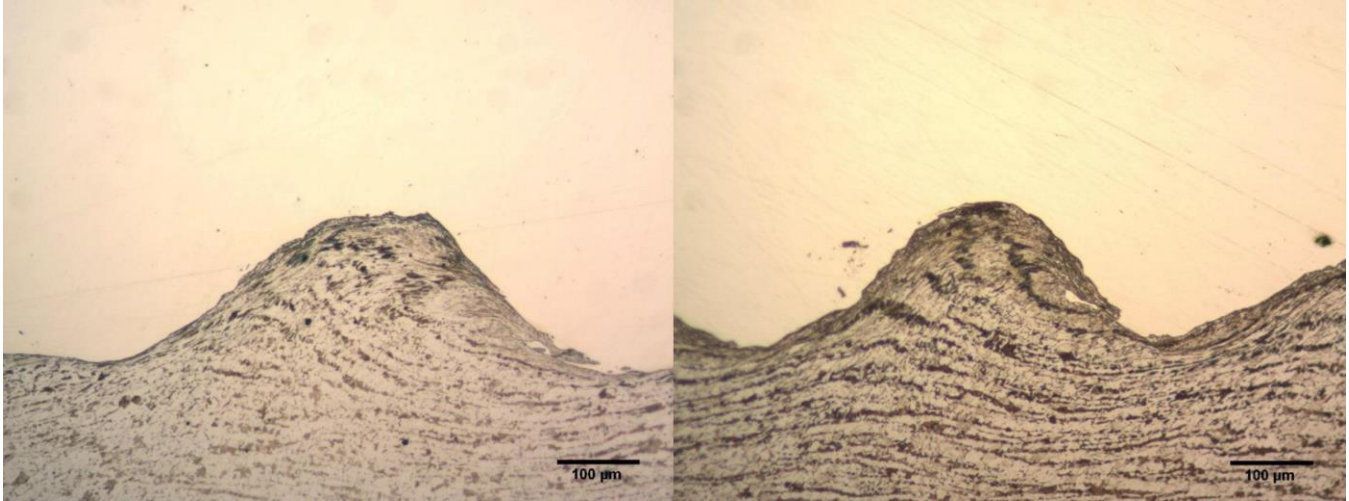
Figure 7: Metallographic inspection of the explosion cladding interface. On the left-hand side UNS N06059 and on the right-hand side UNS N06058 are shown. They represent a typical interface for the explosion cladding process; Nital etch.

The **metallographic inspection** of the microstructure of both alloys, as shown in Figure 8, reveals equiaxed grains and grain boundaries free of precipitations as well as precipitate free grains. The twinning of several grains is an indicator of a fully recrystallized microstructure. Furthermore, no evidence of excessive cold work is present in the metallographic images.

Figure 8: Metallographic inspection of the microstructure of UNS N06059 (left) and UNS N06058 (right) after explosion cladding.

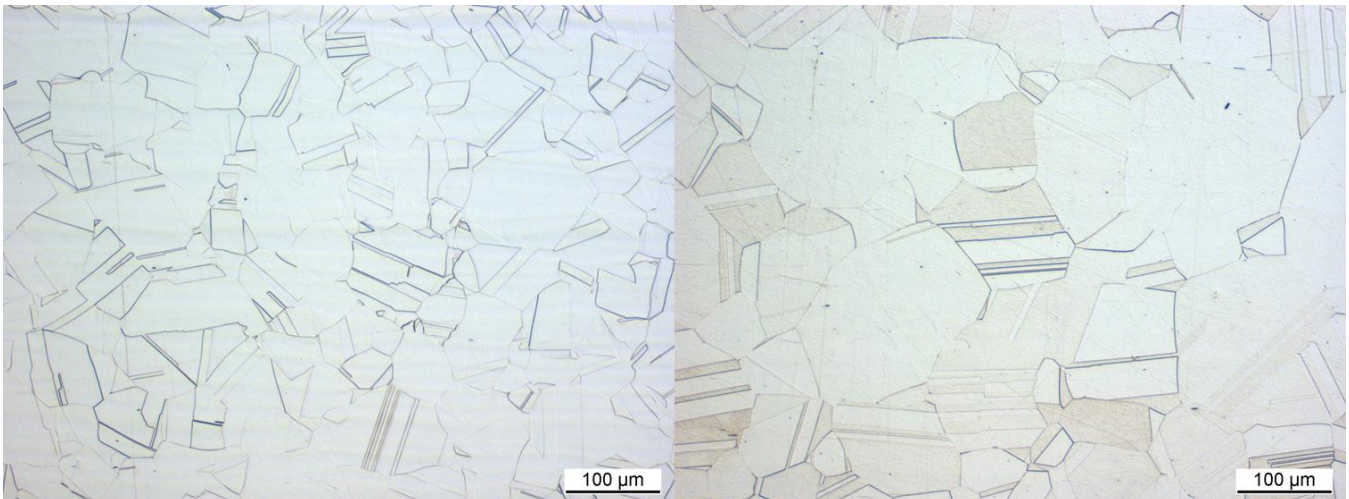## Investigation of mechanical properties

Mechanical testing was performed in terms of a tensile test (base material), shear test (bond) and a bending test (bond). The tests performed according to ASTM SA-265 were compliant with the requirements for the condition *after heat treatment* at 600 °C for 13.5 hours (see Table 4, Table 5 and Table 6). The condition of the specimen represents the maximum stress-relief cycles required for the head forming process to restore the mechanical properties of the base material.

Table 4: Tensile tests in condition *after head forming + heat treatment* (stage 4).

UNS	Specimen / Area	R_M [MPa]	Elongation [%]	Conform
N06059	2 Knuckle	518	32,4	Yes
	3/1 Crown	502	36,4	Yes
N06058	5 Knuckle	518	33,3	Yes
	6/4 Crown	499	31,6	Yes

Table 5: Shear tests in condition *after head forming + heat treatment* (stage 4).

UNS	Specimen / Area	R_M [Mpa]	Conform
N06059	2 Knuckle	446	Yes
	3/1 Crown	530	Yes
N06058	5 Knuckle	503	Yes
	6/4 Crown	552	Yes

Table 6: Bending test in condition *after head forming + heat treatment* (stage 4).

UNS	Specimen / Area	Conform
N06059	2 Knuckle area	Yes
	3/1 Crown area	Yes
N06058	5 Knuckle area	Yes
	6/4 Crown area	Yes

Investigation of Corrosion resistance

Corrosion testing was performed in green death solution, in ASTM G28 A medium as well as in 10 % HCl and 50 % H_2SO_4. For this purpose, duplicates for each tested condition and medium were used. To determine the mass loss rates, the results of the two specimens with respect to each condition/location were averaged with error indicators.

The results of the investigation of critical pitting temperature are shown in Table 7. Compared to the solution annealed condition, the explosion cladding and head forming process as well as the applied heat treatment did not have any impact on the resistance against pitting corrosion in either material. Furthermore, UNS N06058 showed, as expected, a higher critical pitting temperature in contrast to UNS N06059 due to its higher PRE number.

Table 7: Results from investigations on critical pitting temperature of UNS N06058 and UNS N06059 in conditions *solution annealed*, *after head forming* and *after head forming + heat treatment*.

UNS	Specimen / Area	Condition	CPT [°C]
N06059	Plate	Solution annealed	135
	2 Knuckle area	After head forming	140
	2 Knuckle area	After head forming + heat treatment	135
N06058	Plate	Solution annealed	>145
	5 Knuckle area	After head forming	>145
	5 Knuckle area	After head forming + heat treatment	>145

According to prior investigations[21], the composition of UNS N06059, with respect to the Cr/(Mo+W) ratio, should be more thermally stable than UNS N06058. The function of the compositional ratio shown in Figure 9 depicts the estimated corrosion behavior in the oxidizing test solution used for ASTM G28 A (50 % H_2SO_4 + 42 g/l $Fe_2(SO_4)_3$ x $9H_2O$, boiling). As can be seen in Figure 10 and Table 8, both alloys, regardless of condition or location, perform according to the calculated function.
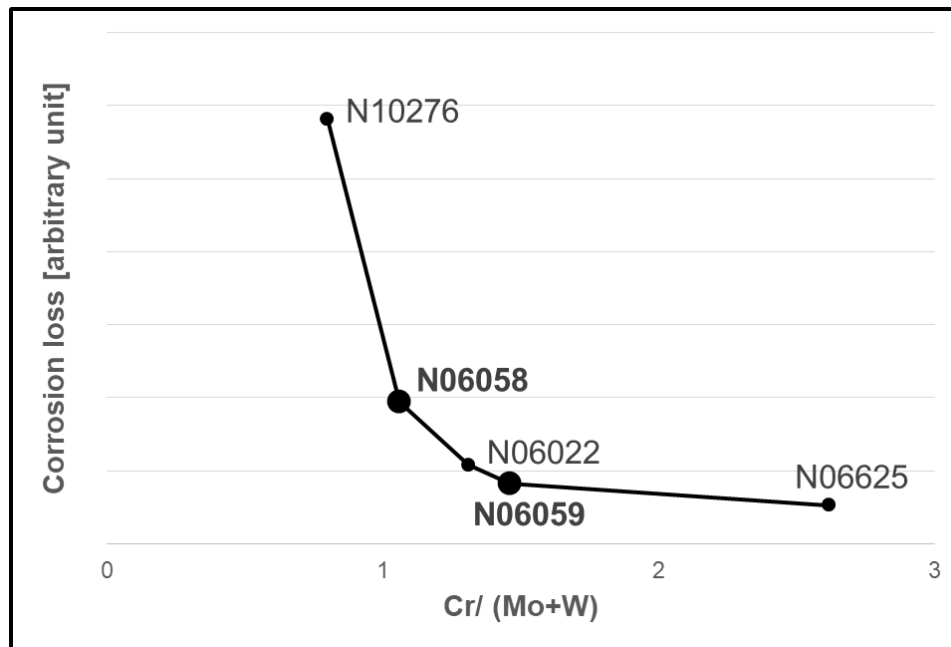

Figure 9: Corrosion loss of selected alloys as a function of their Cr/(Mo+W)-ratio after testing according to ASTM G28 A taken from[21] and extended by UNS N06058.

Further, the results for ASTM G 28 A indicate no evidence of sensitization for any material or condition. The calculated mass loss rates of both materials and all the tested conditions seem equivalent to the solution annealed condition.

Furthermore, when looking at the data presented, it is evident that UNS N06059 shows an intergranular corrosion attack lower than UNS N06058 regardless of its heat treatment condition or the specimen's location.

Using the mentioned parameters for explosion cladding, head forming and the lower temperature of 600 °C for post weld heat treatment, a sensitization of the microstructure could be prevented.
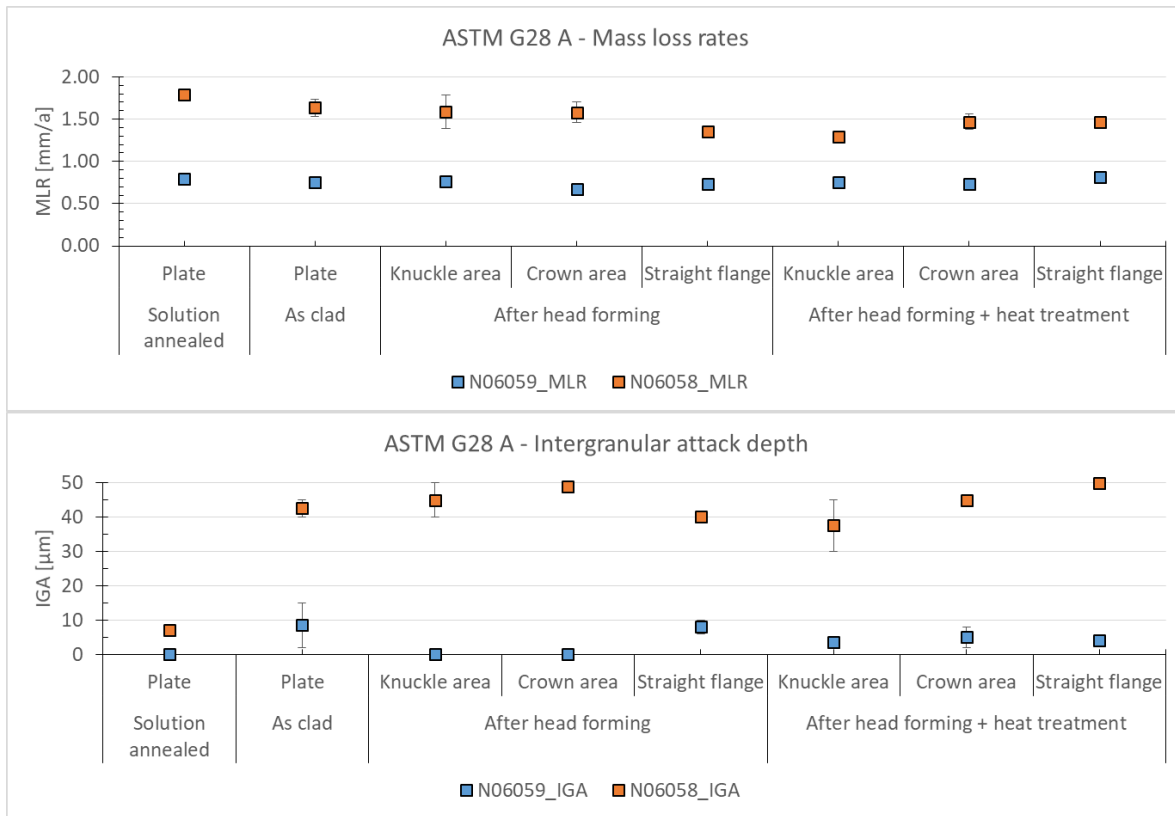
Figure 10: Results for ASTM G28 A test with a testing period of 24 hours. The mass loss rate (MLR) in mm per anno and the intergranular attack depth (IGA in μm) are shown in the diagrams with respect to the tested condition and sample location

Table 8: Detailed overview of the test results according to ASTM G28 A. The averaged value of the mass loss rate (MLR) and the intergranular corrosion attack depth (IC-depth) are shown with respect to the specimen's condition and location.

UNS	Condition	Location	MLR [mm/a]	IC-depth [μm]
N06059	Solution annealed	Plate	0.79	0
	As clad	Plate	0.75	8.5
	After head forming	Knuckle area	0.76	0
		Crown area	0.68	0
		Straight flange	0.73	8
	After head forming + heat treatment	Knuckle area	0.75	3.5
		Crown area	0.73	5
		Straight flange	0.81	4
N06058	Solution annealed	Plate	1.79	7
	As clad	Plate	1.64	42.5
	After head forming	Knuckle area	1.59	45
		Crown area	1.58	49
		Straight flange	1.36	40
	After head forming + heat treatment	Knuckle area	1.29	37.5
		Crown area	1.47	45
		Straight flange	1.47	50

Further testing was performed in 10 % hydrochloric acid at 60 °C and 50 % sulfuric acid at 100 °C for 24 hours each. The results are shown in Figure 11 and Table 9.
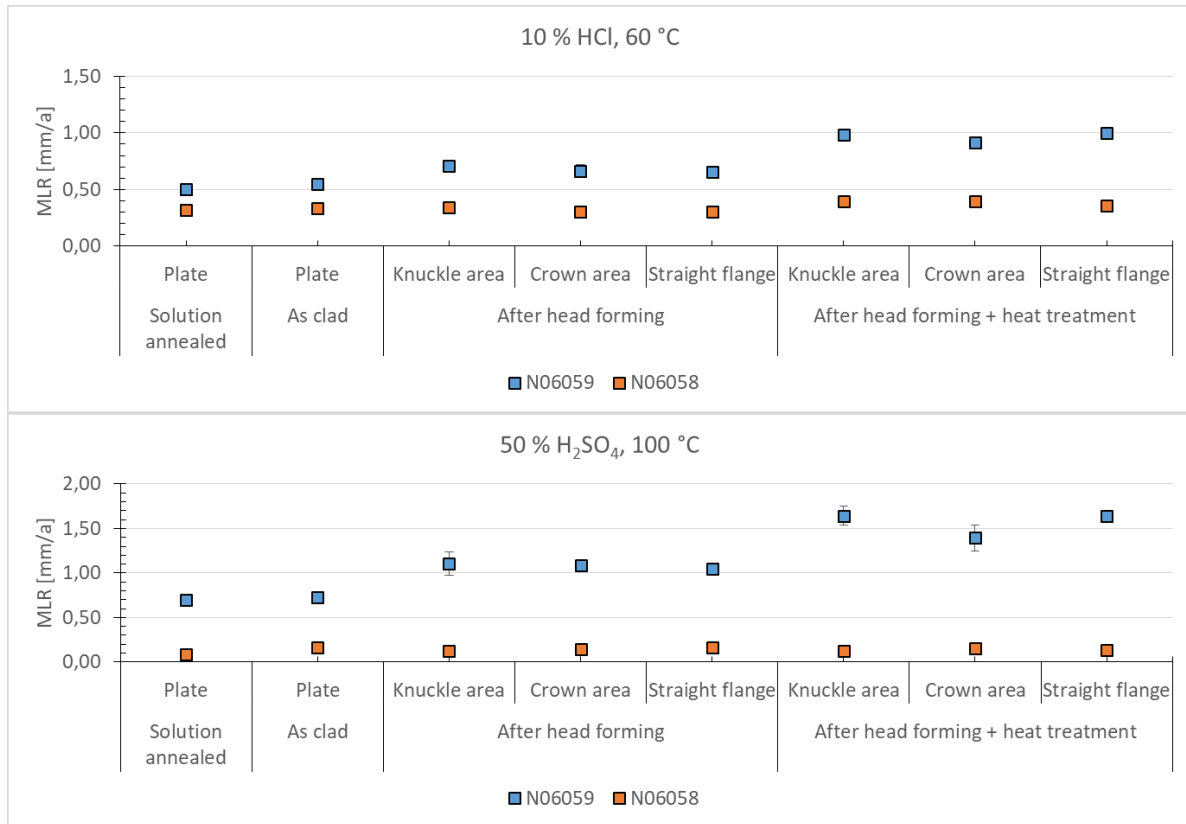

Figure 11: The mass loss rates of the specimen tested in hydrochloric acid at 60 °C and in 50 % sulfuric acid at 100 °C for 24 hours each with respect to their condition and location.

Table 9: Detailed overview of mass loss rates (MLR) measured in 10 % HCl at 60 °C and in 50 % H_2SO_4 at 100 °C. The average MLR's are depicted with respect to the specimen's condition and location.

UNS	Condition	Location	10 % HCl, 60 °C MLR [mm/a]	50 % H_2SO_4, 100 °C MLR [mm/a]
N06059	Solution annealed	Plate	0,51	0,70
	As clad	Plate	0,55	0,73
	After head forming	Knuckle area	0,71	1,11
		Crown area	0,67	1,08
		Straight flange	0,66	1,04
	After head forming + heat treatment	Knuckle area	0,98	1,65
		Crown area	0,91	1,40
		Straight flange	1,00	1,65
N06058	Solution annealed	Plate	0,32	0,08
	As clad	Plate	0,33	0,17
	After head forming	Knuckle area	0,34	0,13
		Crown area	0,30	0,14
		Straight flange	0,30	0,16
	After head forming + heat treatment	Knuckle area	0,40	0,12
		Crown area	0,40	0,15
		Straight flange	0,36	0,13

10 % hydrochloric acid, 60 °C:

UNS N06058 showed comparable mass loss rates to the solution annealed samples under all tested conditions and at all locations. Even after the post weld heat treatment at 600 °C for 13.5 hours, which is required by the code to restore the mechanical properties of the base material, the mass loss rate reached only about 0.4 mm/a.

The tested medium represents a strongly reducing acid, in which a high molybdenum content is required to maintain low corrosion rates. Due to the 3 wt.% higher molybdenum content in UNS N06058 compared to UNS N06059, the corrosion rates are not very much affected.

For UNS N06059, on the other hand, it is evident that the used medium represents the limitations of the material regarding corrosion resistance. Even marginal precipitation processes, resulting from the temperatures the material was exposed to, might reduce the molybdenum content of the matrix. Therefore, the elevated corrosion rates observed in Table 9 were to be expected.

The results show differences in mass loss rates compared to the solution annealed condition, revealing that the condition *after head forming + heat treatment* almost doubled in mass loss, reaching about 1 mm/a.

50 % sulfuric acid, 100 °C:

UNS N06058 is significantly more resistant compared to UNS N06059 in the tested reducing medium. The outstanding resistivity of the material is attributed to its higher molybdenum content. Thus, the measured values of UNS N06058 after the explosion cladding process and a simulated post weld heat treatment do not differ much from the solution annealed condition of the material. Even after the post weld heat treatment at 600 °C for 13.5 hours, the mass loss rates are found below 0.2 mm/a.

In contrast, UNS N06059 reaches a mass loss rate of about 0.7 mm/a both in solution annealed condition and after explosion cladding. For the condition *after head forming + heat treatment*, the material showed even higher mass loss rates up to 1.65 mm/a. These high values at a testing temperature of 100 °C do not seem surprising, more so revealing the limitations of the material in this strongly reducing medium. A technical corrosion resistance of about 0.1 mm/a of UNS N06059 in 50 % sulfuric acid is given up to a testing temperature of about 75 °C[22]. Therefore, even minor changes in the microstructure resulting from the temperatures the material was exposed to during processing has negatively influenced the resistance of UNS N06059 in the tested medium.

CONCLUSIONS

- Both alloys UNS N06059 and UNS N06058 can be reliably explosion clad and neither head forming nor a PWHT at 600 °C for 13.5 hours followed by air cooling did cause sensitization of the microstructure according to ASTM G28 A tests.
- Both alloys perform as expected with respect to the element ratio of Cr to Mo + W in the oxidizing medium used in the ASTM G28 A test even *after head forming* and a subsequent PWHT. UNS N06058 has higher mass loss rates and deeper intergranular attacks caused by the faster sensitization behavior.
- Neither explosion cladding nor the head forming process negatively affect the critical pitting temperature of both materials. The measured values in green death solution represent the solution annealed condition.
- For the tests in hydrochloric and sulfuric acid, representing strongly reducing conditions, UNS N06058 showed mass loss rates in the area of the solution annealed condition and significantly lower compared to UNS N06059 for all the tested specimen conditions and at all locations.
- In 10 % hydrochloric acid at 60 °C, UNS N06058 showed mass loss rates in the area of 0.3 mm/a after explosion cladding. A subsequent PWHT at 600 °C for 13.5 hours with air cooling resulted in a mass loss rate ≤ 0.4 mm/a.

- In 50 % sulfuric acid at 100 °C, after explosion cladding, UNS N06058 shows corrosion rates below 0.2 mm/a. After a subsequent PWHT at 600 °C for 13.5 hours with air cooling, the mass loss rate of UNS N06058 stays below 0.2 mm/a.

ACKNOWLEDGEMENTS

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